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(54) A toner powder for the development of latent electrostatic or magnetic images and a process for forming fixed images on an image receiving material.

(57) A toner powder for the development of latent electrostatic or magnetic images, said toner powder containing a polyester resin based on an etherified diphenol and a dicarboxylic acid and the polyester resin being mixed with a reaction product of an epoxy resin and a phenol compound or a carboxylic acid, and a process for forming fixed images on an image receiving material, in which an image is applied to a medium by means of said toner powder, the surface of the medium consisting of material having a lower affinity for the softened toner powder than the image receiving material and the toner powder being softened by heating before and/or during transit through the pressure zone.

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The invention relates to a toner powder for the developm nt of latent electrostatic or magnetic images, said toner powder containing a polyester resin based on an etherified diphenol and a dicarboxylic acid. The invention also relates to a process for fixing toner images made on a receiving support by means of such toner powder.

A toner powder according to the preamble is known from British patent GB-1 373 220.

The thermoplastic resin in this known toner powder is a polyester resin based on an etherified diphenol and a dicarboxylic acid, if required with acids having more than two carboxyl groups or alcohols having three or more hydroxyl groups. It has been found in practice that the preparation of such thermoplastic resins is difficult to control, so that there is a spread in thermal properties. Another disadvantage of the use of such thermoplastic resins is, that despite the fact that the fixing temperature of toner powder prepared with these resins can be reduced by, for example, adapting the molecular weight distribution, the storage stability, for example, is also adversely affected by such adaptation.

In order to function properly, toner powders must satisfy a large number of other requirements.

The conventional method of preparing a toner powder is to mix the constituents in the melt, cool the melt, and then grind and screen it to the correct particle size. The toner must accordingly be well adapted to grinding and satisfy certain requirements in respect of toughness and brittleness. During storage the toner powder must also be stable over a wide temperature range and at extreme relative humidities in order to avoid caking. In addition, the toner powder must not agglomerate under conditions prevailing in a developing device (mixing, high temperature, and so on). It has been found in practice that a glass transition temperature higher than 40 °C is favourable to the avoidance of agglomeration. Deposition of toner resin on a photoconductor affects the photoelectric properties of the photoconductor. Accordingly the toner powder should not leave any non-removable residues on the photoconductor.

The toner image should also be capable of being satisfactorily fixed on a receiving material. The toner image should be so fixed that it is scarcely removed, if at all, under mechanical loads such as folding and rubbing. The fixing temperature in these conditions should be as low as possible in connection with minimum energy consumption.

The working range of a toner powder should, of course, be so wide that any temperature inequalities occurring in the fixing station are taken care of. The working range of a toner powder is defined as the temperature range between the lower fusing limit, the lowest possible fixing temperature at which the toner image is still adequately fixed, and the upper fusing limit, the maximum fixing temperature at which, using for example the hot-roll fixing method, no toner is deposited on the fixing roller (the "hot roll").

It must also be possible to provide both sides of a receiving material with a toner image. With double sided or "duplex" copying, it is conventional practice to provide first one side of the receiving material with a toner image, to fix this toner image on the receiving material, to turn the receiving material over, and then provide the other side with a toner image and fix that toner image. This may cause deposition of toner powder from the toner image on pressure rollers, and this necessitates regular cleaning of such rollers, and may also cause soiling on subsequent copies. During the last fixing step the first toner image fixed must not be subjected to deformation or become detached from the paper. This means that the softening range and the adhesive and cohesive properties of the toner powder must satisfy certain requirements.

Moreover, after the heat treatment, the fixed toner image must rapidly become permanent and lose its tackiness in order to avoid any damage to the toner image on transport through the copying machine.

The object of this invention is to provide a toner powder which satisfies the above requirements and which has the above disadvantages only to a reduced degree, if at all.

This object is attained with a toner powder according to the preamble, characterised in that the polyester resin is mixed with a reaction product of an epoxy resin and a phenol compound or a carboxylic acid. A toner powder of this kind is simple to make, can readily be fixed on a receiving material, and can be made suitable for use at different fixing temperatures and speeds by selecting the resins and ratios. With such toner powder, the lower fusing limit at which the toner image can still be fixed on a receiving material is much lower in comparison with the lower fusing limit of toner powder with the same polyester resin without the addition of the reaction product.

Usable epoxy resins, for example, are the Epikote resins (Shell), such as Epikote 828,838 and 1001. In addition, many other epoxy resins can be used which contain one or more epoxy groups per molecule. These epoxy resins are saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, and may be substituted with substituents such as halogen atoms, hydroxyl groups, alkyl, aryl or alkaryl groups, alkoxy groups and the like. The phenol compounds suitable in the toner powder according to the invention are those compounds which have at least one hydroxyl group bonded to an aromatic nucleus. Mainly etherification takes place on reaction between the epoxy resin and the phenol compound. A reaction of this kind is also known as blocking.

Examples of suitable phenols are phenol, 2,2-bis(4-hydroxyphenyl)-propane, o-tert.butylphenol, p-sec. butylphenol, octylphenol, p-cyclohexylphenol, α-naphthol and β-naphthol. Other blocking agents, for example, monofunctional carboxylic acids, ar also suitable.

Examples of suitable carboxylic acids are phenylacetic acid, diphenylacetic acid and p-tert.butylbenzoic acid.

The selection of a specific polyester resin depends on the required use of the toner powder. Linear polyester resins based on the diols and dicarboxylic acids as described in GB-1 373 220 are suitable for use in the toner powder according to the invention. Although not preferred, branched polyester resins as described in GB-1 373 220 are also suitable within certain limits. The suitability in such cases depends inter alia on the miscibility of the polyester resin and the reaction product of the epoxy resin and the phenol compound or the carboxylic acid.

Suitable diols are, inter alia, etherified bisphenols, such as polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane, polyoxypropylene(3)-2,2-bis(4-hydroxyphenyl)-propane, polyoxypropylene(3)-bis(4-hydroxyphenyl)-sulphone, polyoxyethylene(2)-bis(4-hydroxyphenyl)-sulphone, polyoxypropylene(2)-bis(4-hydoxyphenyl)-thioether and polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl)-propane or mixtures of these diols, in which a plurality of oxyalkylene groups per molecule of bisphenol may be present. This number is preferably between 2 and 3 on average. It is also possible to use mixtures of etherified bisphenols and (etherified) aliphatic diols, triols, etc. Examples of suitable carboxylic acids are phthalic acid, terephthalic acid, isophthalic acid, cyclohexane dicarboxylic acid, fumaric acid, maleic acid, malonic acid, succinic acid, glutaric acid, adipic acid and anhydrides of these acids. Furthermore esters, e.g. methyl esters of these carboxylic acids, are suitable.

It should be mentioned here that toner powders based on mixtures of polyesters and epoxy resins are known per se. US-A-4,693,952 describes a toner powder which comprises a polyester resin and an epoxy resin such as, for example, Epikote 1004. However, due to the presence of reactive epoxy groups, a toner resin of this kind is mutagenic in the Ames test and also unstable in time. Also, branching of the polyester is necessary in order to avoid deposition of toner resin on hot parts of the fixing device and owing to the softening temperatures of the toner powders high fixing temperatures are necessary.

Preferably, a toner powder is used characterised in that the polyester resin has a number-averaged molecular weight of at least 2500, the epoxy resin has a number-averaged molecular weight of less than 1200 and the epoxy groups of the epoxy resin are blocked for at least 60% by a phenol compound. Both resins are well miscible and the resulting toner powder has favourable thermal properties.

The reaction product of the epoxy resin and the phenol compound preferably contains less than 50 mmol free epoxy groups per kg of reaction product. By allowing the epoxy groups remaining after etherification or blocking with the monofunctional phenol compound to react, the reaction product has practically no reactive epoxy groups, so that the stability of the toner powder produced therewith is improved and the toner powder is not mutagenic in the Ames test. For use as a coloured toner powder, for example, it is advantageous if the epoxy groups of the epoxy resin are blocked for at least 80% by th monofunctional phenol compound. With such a degree of blocking, in fact, relatively clear resins are obtained.

Particularly preferred is a toner powder which is characterised in that the polyester resin is mixed with a reaction product of an epoxy resin containing mainly the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)-propane and a monofunctional phenol compound. One example of such an epoxy resin is Epikote 828 (Shell). The reaction product of such an epoxy resin can be prepared with very constant properties so that the variation in thermal properties of the toner powder made therewith is reduced.

In toner powders according to the invention, the polyester resin : reaction product of the epoxy resin and phenol compound ratio may be varied between 80 : 20 and 20 : 80. Toner powders of this kind have a sufficiently wide working range. The temperature difference between the glass transition temperature and the lower fusing limit of the toner powders according to the invention is also significantly reduced in comparison with the temperature difference between the glass transition temperature and the lower fusing limit of toner powder prepared with polyester resin without the addition of the epoxy reaction product. Consequently, while powder stability is retained the fixing temperature of such toner powders is lower so that the energy consumption for fixing is reduced.

Preferably, the toner powder according to the invention is also characterised in that the polyester resin : reaction product of the epoxy resin and phenol compound ratio is between 60 : 40 and 30 : 70. Toner powders of this kind are in practice less sensitiv to variations in visco-elastic properties of the higher molecular polyester resin. As a result, the requirements to be satisfied in respect of the polyester resin product constancy are reduced.

In practice it has been found favourable if the glass-transition temperature of th reaction product of the

epoxy resin and th phenol compound is above 35 °C. Toner powders comprising such a reaction product have hardly any agglomeration problems, if any, on storage. Preferably, the glass-transition temperature of the reaction product of the epoxy resin and the phenol compound is above 45 °C. As a result of the high glass transition temperature it is possible to make toner powders in which the mixing ratios can be selected freely within wide limits for uses at different fixing temperatures and speeds.

Preferably, the polyester resin is mainly a reaction product of one or more alkoxylated bisphenol compounds and one or more aromatic and/or fully saturated dicarboxylic acids or their corresponding esters. As contrasted with toner powders in which polyesters with reactive groups such as unsaturated bonds are present, toner powders prepared with such a resin have improved stability so that hardening on hot components is virtually prevented. Particularly preferred is a toner powder whose polyester resin is mainly a reaction product of ethoxylated 2,2-bis(4-hydroxyphenyl)propane and phthalic acid or a phthalic acid ester. A toner powder of this kind has a sufficiently high glass transition temperature and also a surprisingly low lower fusing limit, so that the energy required to fix a toner image prepared with this toner powder is relatively low.

The invention also relates to a process for forming fixed images on an image receiving material, in which an image is applied to a medium by means of toner powder containing thermoplastic resin, the surface of the medium consisting of material having a lower affinity for the softened toner powder than the image receiving material and the toner powder being softened by heating before and/or during transit through the pressure zone. A process of this kind is described inter alia in British patent 1 245 425 and United States patents 3 554 836 and 3 893 761. In these processes, a powder image formed, for example, on a photoconductive or magnetisable image recording material is transferred, by the application of pressure, to a medium whose surface consists of a material having a low affinity for the softened powder, e.g. silicone rubber. The powder image is then again transferred, by pressure application, to an image receiving material, the powder being softened by heating before and/or during transit through the pressure zone, so that it acquires properties such that as a result of the pressure applied it forms a cohesive layer which penetrates at least partially into the image receiving material. After cooling the image is durably bonded to the receiving material. For use in this process the toner powders proposed heretofore include those which contain polyesters, polystyrene or epoxy resin as a thermoplastic resin. Using such toner powders it is possible to embody working systems, but it has been found that these systems have deficiencies. One of the disadvantages is that the working range continually decreases and after some tens of thousands of imaging cycles the medium reaches a situation in which there is no practical working range. Thermal degradation of the medium probably plays a part in this.

Another disadvantage in practice is that the material deposited on the medium is partly returned to the image recording material by the medium so that it is rendered unsuitable for further use.

In order to considerably reduce these disadvantages the invention provides a process as indicated above, which is characterised in that the image is applied by means of a toner powder containing a polyester resin based on an etherified diphenol and a dicarboxylic acid and the polyester resin of which is mixed with a reaction product of an epoxy resin and a phenol compound. It has been found in practice that when such a toner powder is used in the process according to the invention the working range remains reasonably constant even after many tens of thousands of imaging cycles.

The exact position and size of the working range are determined, not only by the properties of the toner powder itself, but also by the geometry of the device in which the process according to the invention is performed, the speed at which the device operates, the composition and hardness of the medium to which the toner powder is applied imagewise, the way in which the toner powder is softened and the pressure with which the softened toner powder is transferred to the image receiving material. The contact time, in particular, between the medium bearing the powder image and the image receiving material is a factor which considerably governs the working range.

The working range can readily be determined for a specific device by measuring the temperature range within which complete transfer and good adhesion of the powder image are obtained. A resonable indication of the position and size of the working range of a specific toner powder can be obtained by measuring the visco-elastic properties of the toner powder. Generally speaking, the working range of the toner powder corresponds to the temperature range within which the loss compliance (J") of the toner powder, measured at a frequency equal to 0.5 times the reciprocal of the contact time in the device used for performing the process according to the invention, is between 10^{-4} and 10^{-6} m^2/N.

The visco-elastic properties of the toner powder are measured in a rheometer, the moduli G' and G" being determined as a function of the frequency at a number of different temperatures. The curves found are then reduced to one curve at one temperature, the reference temperature. From this reduc d curve the loss compliance (J") is calculated as s function of the frequency. The displacement factors of the lower fusing

limit and upper fusing limit temperatures (J'' = 10^{-5} and 10^{-4} m^2/N respectively) of the working range can then be read off from the loss compliance-frequency-curve. The lower and upper fusing limit temperatures of th working range can then be calculated by means of the WLF equation compiled from the displacement factors found at different temperatures.

The weight-averaged molecular weight of the polyester and epoxy resins is determined by GPC measurement with UV and refractive index detection.

In addition to thermoplastic resin, the toner powder also contains colouring material, which may consist of carbon black or inorganic or organic pigment or dye. The toner powder may also contain other additives, the nature of which depends on the way in which the toner powder is applied. Thus toner powder for the development of latent magnetic images, toner powder which is fed by magnetic conveying means to an electrostatic image to be for developed, or toner powder for Magnetic Ink Character Recognition (MICR) applications, will also have to contain magnetisable or magnetic material, usually in a quantity of 30 to 70% by weight. Toner powders which are used for the development of electrostatic images may also be rendered electrically conductive in manner known per se, by finely distributing electrically conductive material, e.g. carbon, tin oxide, copper iodide or any other suitable conductive material, in appropriate quantity in the powder particles or depositing it on the surface of the powder particles. If, for the development of electrostatic images, the toner powder is used in a so-called two-component developer, in which the toner powder is mixed with carrier particles, then the toner powder particles may also contain a charge control agent that causes the toner powder particles, upon tribo-electric charging, to assume a charge whose polarity is opposed to that of the electrostatic image to be developed. The known materials suitable for this purpose can be used as carrier particles, e.g. iron, ferrite or glass, while the particles may be provided with one or more layers completely or partially covering the carrier particles.

It has been found in practice that the toner powders according to the invention are satisfactorily usable in a two-component developer, inter alia because of the very good impact strength and resistance to wear (abrasion resistance) of the toner powder particles. In particular it was found that the use of the toner powder according to the invention reduced the progressive deterioriation of the triboelectric charging properties significantly.

The known materials may be used for the magnetisable or magnetic material, electrically conductive material or charge control agent. Also possible are additions, for example, to increase the powder stability or improve the flow behaviour. Silica is a conventional additive for this purpose for example. Other thermoplastic resins known for use in toner powders can also be used as an additive in the toner powder according to the invention. Examples of such resins are, inter alia, vinyl resins, polyurethane resins, cellulose resins and polyamide resins.

In electrophotography and electrography a latent electrostatic image is formed in known manner on an image support. Thus in electrophotography a photo-conductor surface is charged and then exposed image wise and in electrography the charge is applied image wise to an image support. The latent electrostatic image is then developed to form a visible image using toner powder. This is done, inter alia, by means of known development methods such as magnetic brush development, cascade development and powder cloud development. The toner image can then be fixed directly onto the image support or, as in the case of indirect electrophotography and magnetography, be transferred to a receiving material and be fixed there in known manner, e.g. under the infuence of heat (the radiation fixing method), under the influence of heat and pressure (the hot-roll fixing method), under the influence of microwave radiation or by means of flash fixing.

The invention will be explained in detail with reference to the following examples.

Example 1

For the preparation of the reaction product of an epoxy resin and a phenol, 100 parts of Epikote 828 and 72.5 parts of p-phenylphenol were mixed with one another at a temperature of 105 °C in a reaction vessel, after which 0.1 part of an alkali halide catalyst was added. A process of this kind is described inter alia in US-A-3 978 027. The mixture was then heated for 5 hours at 150 °C, after which the reaction mixture was heated for another 2 hours at 200 °C to react away the remaining epoxy groups. In this way a relatively clear resin was obtained with a glass transition temperature (Tg) of 48.5 °C and a free epoxy group content of less than 40 mmol per kg of reaction product.

Example 2

30 parts of a reaction product of Epikote 828 and p-phenylphenol from Example 1 and 20 parts of polyester resin based on polyoxyethylene (2)-2,2-bis(4-hydroxyphenyl)-propane and dimethylphthalate, with a Tg of

61 °C (Mn 8000) and 50 parts of magnetic pigment (Bayferrox 318 M of Bayer A.G.) were kneaded intensively at a temperature of 105 °C for 2 hours. The mixture was then processed in known manner by grinding and screening to give a toner powder having particles between 10 and 30 µm. The toner powder was then rendered conductive with carbon black using the process of NL-B-168347 (resistance 2.3 x 10^{-5} ohm.m). The resulting toner powder was used in an electrophotographic copying machine as described in EP-A-045 102. The toner image obtained in known manner was applied to a medium consisting of a steel roller having a cross-section of 100 mm, to which a 1.7 mm thick pigmented RTV silicone rubber layer had been applied, said layer also being provided with an RTV top layer of 50 µm in accordance with NL-A-8801669. This medium provided with the toner image was heated and brought into contact at a linear pressure of 1500 N/m with a receiving material heated to 92 °C. Océ plain paper was used as receiving material. The lower fusing limit at which the toner powder was sufficiently fixed to the paper was found to be 86 °C and the working range was about 19 °C. The Tg of the resin mixture of the toner powder was 51 °C. For comparison, a toner powder prepared in the identical manner and having, as thermoplastic resin, a polyester resin based on maleic acid anhydride and polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl)-propane with a Tg of 53.5 °C, was used in the same apparatus. With this toner powder the lower fusing limit was 104 °C while the working range was 17 °C.

Example 3

Three toner powders were prepared with a thermoplastic resin containing 60% by weight of the reaction product from Example 1 and 40% by weight of polyester resin based on polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane and dimethylphthalate, with different number-averaged molecular weights (Mn). The results of the lower fusing limits determined by measurements of the visco-elastic properties, and working ranges, of the toner powders are given in the following table.

Toner powder	Mn	Lower fusing limit(°C)	Working range width
3a	8000	91	19
3b	6000	87	16
3c	3000	81	13

With a lower Mn, the width of the working range becomes too small for practical use, because of temperature inequalities in fixing devices, spreads in temperature adjustments of different fixing devices, and the like.

Example 4

Three toner powders were prepared in accordance with Example 2 with a thermoplastic resin containing 60% by weight of the reaction product of Epikote 828 (Shell) and p-phenylphenol and 40% by weight of polyester resin from Example 2, the epoxy resin being etherified or blocked with 70, 80 and 90% p-phenylphenol as in Example 1. The results of the lower fusing limits determined by measurements of the visco-elastic properties, and working ranges, of the toner powders are given in the following table.

Toner Powder	Degree of blocking	Tg	Lower fusing limit (°C)	Working range width	Colour
4a	70	54	87.5	19	Brown
4b	80	51.5	84.5	18.5	Relatively clear
4c	90	50	82	18	Relatively clear

Toner powders in which the degree of blocking is 80% or higher are relatively clear and hence favourable, for example, for colour toner applications.

Example 5

Toner powders were prepared in accordance with Example 2 with a thermoplastic resin mixture containing in different proportions a polyester based on polyester resin based on maleic acid anhydride and

polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl)-propane and the reaction product of 100 parts of Epikote 828 (Shell) and 90 parts of p-cumylphenol prepared in accordance with Example 1. The reaction product had a Tg of 35.5 °C. The results of the lower fusing limits determined by measurements of the visco-elastic properties, and working ranges, of the toner powders are given in the following table.

Toner powder	Reaction product % by weight	Tg mixture	Lower fusing limit (°C)	Working range width
5a	0	54.5	104	19.5
5b	10	51	99.5	19.5
5c	20	49	93.5	19.5
5d	30	46	87.5	18
5e	40	44	83.5	17
5f	50	41	78	16

It will be clear from this table that the lower fusing limit falls sharply with increasing reaction product content while the working range remains sufficiently wide.

Example 6

Toner powders were prepared similarly to Example 5 with a thermoplastic resin mixture containing in different proportions a polyester resin based on polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane and dimethylphthalate, with a Tg of 57 °C and the reaction product of Example 1. The reaction product had a Tg of 49 °C. The results of the lower fusing limits determined by measurements of the viscoelastic properties, and working ranges, of the toner powders are given in the following table.

Toner powder	Reaction product % by weight	Tg mixture	Lower fusing limit (°C)	Working range width
6a	0	57	117.5	25
6b	20	54,5	105.5	23.5
6c	40	54	94.5	20.5
6d	60	51	87.5	16
6e	80	49	81.5	12.5

It will be seen from these results that the ratio of reaction product to polyester can be varied within wide limits with a reaction product Tg of 49 °C while retaining a sufficiently wide working range. The toner powders having a reaction product % by weight of 40 - 60% are particularly favourable because of the combination of the relatively wide working range and the low lower fusing limit

Example 7

Four toner powders were prepared with a thermoplastic resin containing 40% by weight of the reaction product from Example 1 and 60% by weight of polyster resin based on polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane and respectively dimethylphthalate (A), dimethylterephthalate (B), dimethylisophthalate (C) and a 30 : 70 mixture of adipic acid and terephthalic acid (D). The results of the lower fusing limits determined by measurements of the viscoelastic properties, and working ranges, of the toner powders are given in the following table.

Toner powder	Polyester	Tg polyester	Tg mixture	Lower fusing limit (°C)	Working range width
7a	A	61	51.5	97.5	25
7b	B	72	58.5	104.5	23
7c	C	65	56.5	106.5	22
7d	D	60	51	91	18

Example 8

Toner powders were prepared in accordance with Exampl 2 with a thermoplastic resin containing 60% by weight of the reaction product of Epikote 828 (Shell) and a phenol compound or carboxylic acid and 40% by weight of polyester resin from Example 2, Epikote 828 (Shell) being etherified or blocked in accordance with Example 1 with, respectively, p-phenylphenol (E), o-phenylphenol (F), p-cumylphenol (G), 2,4 di-tert. butylphenol (H), p-cyclohexylphenol (I), α-naphthol (J), β-naphthol (K) or diphenylacetic acid (L) and the remaining free epoxy groups were reacted away by heating to high temperature as in Example 1. The results of the lower fusing limits determined by measurements of the viscoelastic properties, and working ranges, of the toner powders are given in the following table.

Toner powder	Phenol	Tg reaction product	Tg mixture	Lower fusing limit	Working range width
8a	E	49	51.5	84	18.5
8b	F	37	43	76.5	18.5
8c	G	35.5	42.5	74.4	19.5
8d	H	49.5	48	84.5	16
8e	I	41	44.5	78.5	18
8f	J	46	50.5	86	19
8g	K	44.5	49	87.5	19
8h	L	31	42	87	22

Example 9

Toner powders were prepared in accordance with Example 2 with a thermoplastic resin containing 60% by weight of the reaction product of Epikote 828 (Shell) and p-phenylphenol and 40% by weight of polyester resin based on polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)-propane and a 30 : 70 mixture of adipic acid and terephthalic acid, using polyester resins with an MFI (melt flow index) of 1.1 and 2.1 g/min respectively at 125 °C. The resulting toner powders were used in an electrophotographic copying machine as described in Example 2. The various toner powders had an identical lower fusing limit of 85 °C. For comparison, two toner powders were prepared in accordance with Example 2 based on a polyester resin based on maleic acid anhydride and polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl)-propane with MFI's of 0.9 and 1.9g/min respectively at 105 °C. A difference of 7 - 8 °C in the lower fusing limit was found between these toner powders.

Example 10

A toner powder was prepared by melt blending 91% by weight of thermoplastic resin, containing 40% by weight of the reaction product of Epikote 828 (Shell) and p-phenylphenol from Example 1 and 60% by weight of the polyester resin of Example 2, 6% by weight of Printex 35 (Degussa) and 3% by weight of Bontron N-04 nigrosine dye (Orient Chemical, Japan).
The resulting mixture was processed in known manner by cooling and subsequent grinding and screening to give a toner powder having particles between 6 and 16 µm. The particles were subsequently mixed thoroughly with 0.25% by weight of hydrophobic silica (Aerosil R972, Degussa) 1 part of this toner powder was then added to 30 parts of ferrite carrier particles (magnetite, particle size 75-120 µm from Höganäs, Sweden). The carrier particles were coated with 0.25% of a polyvinylidene fluoride resin, in a manner well known in the art.
The mixture of toner particles and carrier particles was then used in a standard electrographic device wherein the toner particles were triboelectrically charged. The charge present on the toner particles was 18 µC/g. Even after prolonged use of the carrier particles the triboelectric charge remained essentially constant. After 20000 imaging cycles a charge of 16 µC/g was found on the toner particles.

Example 11 (comparative)

A mixture composed of toner particles and carrier particles was prepared according to Example 10 using as a thermoplastic resin the polyester resin of Example 5. After triboelectric charging the charge present on the toner particles was 18 µC/g. After 20000 imaging cycles the charge on the toner was 10 µC/g.

Claims

1. A toner powder for the development of latent electrostatic or magnetic images, said toner powder containing a polyester resin based on an etherified diphenol and a dicarboxylic acid, characterised in that the polyester resin is mixed with a reaction product of an epoxy resin and a phenol compound or a carboxylic acid.

2. A toner powder according to claim 1, characterised in that the polyester resin has a number-averaged molecular weight of at least 2500, the epoxy resin has a number-averaged molecular weight of less than 1200 and the epoxy groups of the epoxy resin are blocked for at least 60% by a monofunctional phenol compound.

3. A toner powder according to claim 2, characterised in that the epoxy groups of the epoxy resin are blocked for at least 80% by the phenol compound.

4. A toner power according to one or more of the preceding claims, characterised in that the polyester resin is mixed with a reaction product of an epoxy resin containing mainly the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane and a monofunctional phenol compound.

5. A toner powder according to one or more of the preceding claims, characterised in that the polyester resin : reaction product ratio of the epoxy resin and phenol compound is between 80 : 20 and 20 : 80.

6. A toner powder according to claim 5, characterised in that the polyester resin : reaction product ratio of the epoxy resin and phenol compound is between 60 : 40 and 30 : 70.

7. A toner powder according to one or more of the preceding claims, characterised in that the glass-transition temperature of the reaction product of the epoxy resin and the phenol compound is above 35 °C.

8. A toner powder according to one or more of the preceding claims, characterised in that the glass-transition temperature of the reaction product of the epoxy resin and the phenol compound is above 45 °C.

9. A toner powder according to one or more of the preceding claims 1 to 6, characterised in that th polyester resin is mainly a reaction product of one or more alkoxylated bisphenol compounds and one or more aromatic and/or fully saturated dicarboxylic acids or their corresponding esters.

10. A toner powder according to claim 9, characterised in that the polyester resin is mainly a reaction product of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane and one or more dicarboxylic acids from the following series: phthalic acid, terephthalic acid, isophthalic acid or the corresponding esters of these acids, or a reaction product of polyoxyethylene(2)-2,2-bis(4-hydroxyphenyl)propane and one or more of these carboxylic acids or the corresponding esters and adipic acid.

11. A process for forming fixed images on an image receiving material, in which an image is applied to a medium by means of toner powder containing thermoplastic resin, the surface of the medium consisting of material having a lower affinity for the softened toner powder than the image receiving material and the toner powder being softened by heating before and/or during transit through the pressure zone, using a toner powder according to one or more of the preceding claims 1 to 10.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 0710

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 405 (P-1100)(4348) 31 August 1990 & JP-A-2 156 253 (RICOH CO LTD) 15 May 1990 * abstract *	1,5,9,11	G03G9/087
X	PATENT ABSTRACTS OF JAPAN vol. 15, no. 158 (P-1193)(4686) 19 April 1991 & JP-A-3 028 858 (RICOH K.K.) 7 February 1991 * abstract *	1,5,9,11	
Y	GB-A-2 014 325 (OCE-VAN DER GRINTEN N.V.) * claims; example 7 *	1-9,11	
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 91 (P-558)(2538) 23 March 1987 & JP-A-61 241 765 (HITACHI LTD) 28 October 1986 * abstract *	1-9,11	
Y	WORLD PATENTS INDEX LATEST Week 0486, Derwent Publications Ltd., London, GB; AN 86-025052 & JP-A-60 247 251 (KONISHIROKU PHOTO K.K.) 6 December 1985 * abstract *	1-9,11	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 JUNE 1992	D. Hillebrecht

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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